

Tetraaquabis[4-(imidazol-1-yl- κ N³)-benzoato]manganese(II)

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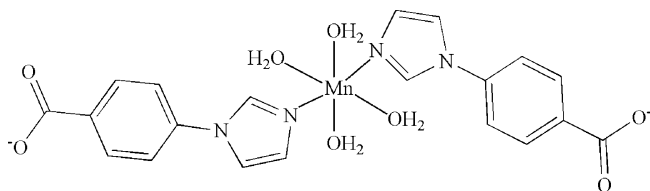
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.113; data-to-parameter ratio = 12.5.

In the title compound, $[\text{Mn}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_4]$, the Mn^{II} atom, lying on an inversion center, has an octahedral environment with four coordinated water molecules in the equatorial plane and two N atoms from two 4-(imidazol-1-yl)-benzoate ligands at the axial sites. The complex molecules are connected into a three-dimensional network by extensive hydrogen bonds between the water molecules and the carboxylate O atoms.

Related literature

For the good coordination ability and diverse coordination modes of ligands containing imidazole and carboxylate groups, see: Fan *et al.* (2004); Sun *et al.* (2005). For the construction of metal-organic frameworks using ligands based on imidazolyl and carboxylate groups as building blocks, see: Carlucci *et al.* (2008); Zhang *et al.* (2007).



Experimental

Crystal data

$[\text{Mn}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_4]$
 $M_r = 501.36$

Monoclinic, $P2_1/c$

$a = 12.278$ (12) Å

$b = 11.026$ (11) Å

$c = 7.978$ (7) Å

$\beta = 96.91$ (2)°

$V = 1072.2$ (18) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.67$ mm⁻¹

$T = 293$ K

$0.28 \times 0.14 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.536$, $T_{\max} = 1.000$

7972 measured reflections

2444 independent reflections

2131 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.113$

$S = 0.91$

2444 reflections

195 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.36$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H13 \cdots O1 ⁱ	0.85 (2)	2.02 (2)	2.837 (3)	161 (2)
O3—H14 \cdots O2 ⁱⁱ	0.79 (3)	1.90 (3)	2.688 (3)	179 (2)
O4—H11 \cdots O1 ⁱⁱⁱ	0.90 (2)	1.82 (2)	2.702 (3)	168 (2)
O4—H12 \cdots O1 ⁱ	0.87 (2)	1.86 (2)	2.694 (3)	158.9 (19)

Symmetry codes: (i) $-x - 1, -y, -z$; (ii) $x + 1, y, z + 1$; (iii) $-x - 1, y - \frac{1}{2}, -z - \frac{1}{2}$.

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2292).

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supplementary materials

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Tetraaquabis[4-(imidazol-1-yl- κ N³)benzoato]manganese(II)

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Comment

Over past few years, considerable effort was paid in the study of metal-organic frameworks (MOFs) owing to their intriguing structural diversity and potential application in adsorption, molecular recognition, catalysis and magnetism. The field of molecular magnets has attracted great interest from different horizons for many years. In this context, the ligand containing imidazole and carboxylate groups is of special interest due to its good coordination ability and diverse coordination modes (Fan *et al.*, 2004; Sun *et al.*, 2005). However, the reports of ligands based on imidazole and carboxylate groups as building blocks for the construction of MOFs (Carlucci *et al.*, 2008; Zhang *et al.*, 2007) are still rare. In this paper, we report the synthesis and structural characterization of the title compound.

As shown in Fig. 1, the molecular structure of the title compound is a mononuclear Mn^{II} complex and the dihedral angle between the imidazolyl ring and the benzene ring of the 4-(imidazol-1-yl)benzoate is 6.3 (2)°. The Mn^{II} ion is coordinated by four water molecules and two N atoms from two different 4-(imidazol-1-yl)benzoate ligands, forming a distorted octahedral coordination environment. The Mn—N and Mn—O bond distances are 2.238 (2) Å and 2.149 (2) and 2.189 (3) Å, respectively. The related hydrogen-bonding geometry is given in Table 1. All values involved with hydrogen bonds fall in a normal range. The intermolecular O—H...O hydrogen-bonding interactions between the coordinated water molecules and carboxylate O atoms of 4-(imidazol-1-yl)benzoate ligands lead to the formation of a three-dimensional network structure as shown in Fig. 2.

Experimental

A 10 ml aqueous solution of 4-(imidazole-1-yl)benzoic acid (0.038 g, 0.20 mmol) was slowly added into the manganese(II) perchlorate (0.663 g, 0.30 mmol) solution in methanol (10 ml). The mixed solution was stirred for 20 min and then HClO₄ solution was added dropwise with constant stirring until the mixed solution was clear. The resulting solution was filtered and the slow evaporation of filtrate in air gave rise to the desirable products, which were subsequently washed twice with Et₂O (yield 38%).

Refinement

All H atoms were located in a difference Fourier map and refined isotropically.

Figures

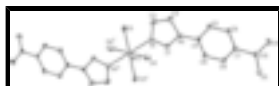


Fig. 1. The molecular structure of the title compound, with the 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry code: (i) -x, -y, -z.]

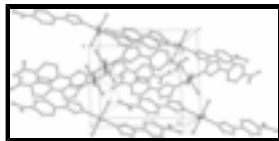


Fig. 2. The crystal packing of the title compound, showing O—H...O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

Tetraaquabis[4-(imidazol-1-yl- κ N³)benzoato]manganese(II)

Crystal data

[Mn(C₁₀H₇N₂O₂)₂(H₂O)₄]

$M_r = 501.36$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.278$ (12) Å

$b = 11.026$ (11) Å

$c = 7.978$ (7) Å

$\beta = 96.91$ (2)°

$V = 1072.2$ (18) Å³

$Z = 2$

$F(000) = 518$

$D_x = 1.553$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3126 reflections

$\theta = 3.3$ – 27.5 °

$\mu = 0.67$ mm⁻¹

$T = 293$ K

Prism, yellow

$0.28 \times 0.14 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.536$, $T_{\max} = 1.000$

7972 measured reflections

2444 independent reflections

2131 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.5$ °

$h = -15 \rightarrow 15$

$k = -14 \rightarrow 13$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.113$

$S = 0.91$

2444 reflections

195 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.36$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.0000	0.0000	0.0000	0.02675 (15)
O1	-0.85062 (8)	0.13841 (11)	-0.33828 (13)	0.0376 (3)
O2	-0.77609 (10)	0.03929 (15)	-0.53834 (16)	0.0491 (3)
O3	0.02777 (12)	0.01354 (13)	0.27549 (16)	0.0452 (3)
O4	-0.07938 (14)	-0.17041 (13)	0.03407 (19)	0.0636 (5)
N1	-0.16150 (10)	0.09039 (13)	0.01711 (16)	0.0364 (3)
N2	-0.33890 (9)	0.12493 (11)	-0.04316 (14)	0.0289 (3)
C1	-0.25122 (12)	0.06006 (16)	-0.0792 (2)	0.0383 (4)
C2	-0.19202 (15)	0.17902 (19)	0.1215 (3)	0.0523 (5)
C3	-0.30063 (15)	0.20096 (19)	0.0867 (3)	0.0550 (5)
C4	-0.44787 (10)	0.11462 (12)	-0.12551 (16)	0.0259 (3)
C5	-0.52854 (12)	0.19507 (14)	-0.08855 (19)	0.0325 (3)
C6	-0.63403 (12)	0.18533 (14)	-0.1733 (2)	0.0332 (3)
C7	-0.65917 (11)	0.09772 (13)	-0.29617 (17)	0.0265 (3)
C8	-0.57766 (14)	0.01717 (15)	-0.3290 (2)	0.0347 (4)
C9	-0.47314 (14)	0.02432 (16)	-0.2445 (2)	0.0372 (4)
C10	-0.77070 (11)	0.09005 (14)	-0.39869 (17)	0.0301 (3)
H1	-0.254 (3)	0.0002 (18)	-0.158 (4)	0.067 (8)*
H2	-0.139 (2)	0.212 (2)	0.210 (3)	0.068 (7)*
H3	-0.347 (2)	0.254 (2)	0.135 (3)	0.070 (7)*
H5	-0.5108 (14)	0.263 (2)	-0.006 (2)	0.047 (6)*
H6	-0.6944 (15)	0.2366 (18)	-0.149 (2)	0.039 (5)*
H8	-0.5940 (17)	-0.048 (2)	-0.418 (3)	0.052 (5)*
H9	-0.4164 (18)	-0.036 (2)	-0.264 (2)	0.048 (5)*
H11	-0.0941 (19)	-0.239 (2)	-0.025 (3)	0.065 (6)*
H12	-0.1116 (17)	-0.1765 (18)	0.126 (3)	0.047 (5)*
H13	-0.016 (2)	-0.035 (2)	0.316 (3)	0.050 (6)*
H14	0.086 (2)	0.021 (2)	0.330 (3)	0.060 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0172 (2)	0.0347 (2)	0.0279 (2)	-0.00251 (9)	0.00068 (13)	-0.00317 (10)
O1	0.0226 (5)	0.0550 (7)	0.0358 (6)	0.0086 (4)	0.0055 (4)	0.0051 (5)
O2	0.0278 (6)	0.0822 (9)	0.0354 (6)	0.0050 (6)	-0.0040 (5)	-0.0161 (6)
O3	0.0302 (7)	0.0748 (9)	0.0294 (7)	-0.0122 (6)	-0.0018 (5)	-0.0016 (5)
O4	0.0892 (11)	0.0500 (8)	0.0604 (9)	-0.0349 (8)	0.0443 (9)	-0.0225 (7)
N1	0.0238 (6)	0.0475 (8)	0.0367 (6)	0.0026 (5)	-0.0010 (5)	-0.0049 (6)
N2	0.0225 (6)	0.0352 (6)	0.0286 (6)	0.0042 (4)	0.0020 (4)	-0.0011 (5)
C1	0.0229 (7)	0.0500 (10)	0.0413 (8)	0.0063 (6)	0.0008 (6)	-0.0125 (7)
C2	0.0345 (9)	0.0640 (12)	0.0547 (11)	0.0065 (8)	-0.0093 (8)	-0.0253 (9)
C3	0.0340 (9)	0.0664 (12)	0.0613 (12)	0.0119 (8)	-0.0084 (8)	-0.0349 (10)
C4	0.0208 (6)	0.0311 (7)	0.0258 (6)	0.0010 (5)	0.0021 (5)	0.0016 (5)
C5	0.0268 (7)	0.0338 (8)	0.0365 (7)	0.0020 (5)	0.0028 (6)	-0.0087 (6)

supplementary materials

C6	0.0240 (6)	0.0356 (8)	0.0404 (8)	0.0066 (5)	0.0062 (6)	-0.0035 (6)
C7	0.0216 (6)	0.0308 (7)	0.0274 (6)	0.0006 (5)	0.0045 (5)	0.0040 (5)
C8	0.0274 (8)	0.0400 (8)	0.0355 (9)	0.0045 (6)	-0.0007 (7)	-0.0098 (6)
C9	0.0268 (8)	0.0413 (8)	0.0425 (9)	0.0105 (6)	0.0004 (7)	-0.0116 (7)
C10	0.0233 (6)	0.0388 (8)	0.0285 (7)	0.0005 (5)	0.0037 (5)	0.0072 (6)

Geometric parameters (Å, °)

Mn1—O4	2.149 (2)	C2—C3	1.351 (3)
Mn1—O3	2.188 (2)	C2—H2	0.97 (2)
Mn1—N1	2.238 (2)	C3—H3	0.93 (3)
O1—C10	1.2623 (19)	C4—C9	1.385 (2)
O2—C10	1.242 (2)	C4—C5	1.387 (2)
O3—H13	0.85 (2)	C5—C6	1.391 (2)
O3—H14	0.79 (3)	C5—H5	1.00 (2)
O4—H11	0.90 (2)	C6—C7	1.385 (2)
O4—H12	0.87 (2)	C6—H6	0.970 (19)
N1—C1	1.308 (2)	C7—C8	1.387 (2)
N1—C2	1.366 (2)	C7—C10	1.511 (2)
N2—C1	1.352 (2)	C8—C9	1.378 (3)
N2—C3	1.371 (2)	C8—H8	1.02 (2)
N2—C4	1.422 (2)	C9—H9	0.99 (2)
C1—H1	0.91 (2)		
O4—Mn1—O4 ⁱ	180.00 (9)	N2—C1—H1	125 (2)
O4—Mn1—O3	87.18 (6)	C3—C2—N1	109.84 (16)
O4 ⁱ —Mn1—O3	92.82 (6)	C3—C2—H2	130.1 (14)
O4—Mn1—O3 ⁱ	92.82 (6)	N1—C2—H2	119.9 (14)
O4 ⁱ —Mn1—O3 ⁱ	87.18 (6)	C2—C3—N2	106.62 (16)
O3—Mn1—O3 ⁱ	180.00 (8)	C2—C3—H3	131.2 (15)
O4—Mn1—N1 ⁱ	92.12 (9)	N2—C3—H3	122.2 (15)
O4 ⁱ —Mn1—N1 ⁱ	87.88 (9)	C9—C4—C5	119.91 (14)
O3—Mn1—N1 ⁱ	93.41 (6)	C9—C4—N2	119.65 (12)
O3 ⁱ —Mn1—N1 ⁱ	86.59 (6)	C5—C4—N2	120.44 (13)
O4—Mn1—N1	87.88 (9)	C4—C5—C6	119.61 (14)
O4 ⁱ —Mn1—N1	92.12 (9)	C4—C5—H5	120.7 (10)
O3—Mn1—N1	86.59 (6)	C6—C5—H5	119.6 (10)
O3 ⁱ —Mn1—N1	93.41 (6)	C7—C6—C5	120.87 (13)
N1 ⁱ —Mn1—N1	180.00 (9)	C7—C6—H6	115.9 (11)
Mn1—O3—H13	108.2 (16)	C5—C6—H6	123.2 (11)
Mn1—O3—H14	125.7 (18)	C6—C7—C8	118.45 (14)
H13—O3—H14	115 (2)	C6—C7—C10	122.20 (13)
Mn1—O4—H11	137.2 (15)	C8—C7—C10	119.32 (14)
Mn1—O4—H12	115.5 (13)	C9—C8—C7	121.45 (15)
H11—O4—H12	107.2 (18)	C9—C8—H8	118.5 (12)
C1—N1—C2	105.52 (14)	C7—C8—H8	120.1 (12)
C1—N1—Mn1	122.68 (12)	C8—C9—C4	119.67 (14)

C2—N1—Mn1	131.77 (11)	C8—C9—H9	121.2 (13)
C1—N2—C3	105.95 (14)	C4—C9—H9	119.1 (13)
C1—N2—C4	126.05 (13)	O2—C10—O1	124.98 (13)
C3—N2—C4	128.00 (13)	O2—C10—C7	117.26 (13)
N1—C1—N2	112.07 (15)	O1—C10—C7	117.73 (14)
N1—C1—H1	123 (2)		

Symmetry codes: (i) $-x, -y, -z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H13...O1 ⁱⁱ	0.85 (2)	2.02 (2)	2.837 (3)	161 (2)
O3—H14...O2 ⁱⁱⁱ	0.79 (3)	1.90 (3)	2.688 (3)	179 (2)
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Symmetry codes: (ii) $-x-1, -y, -z$; (iii) $x+1, y, z+1$; (iv) $-x-1, y-1/2, -z-1/2$.

Fig. 1

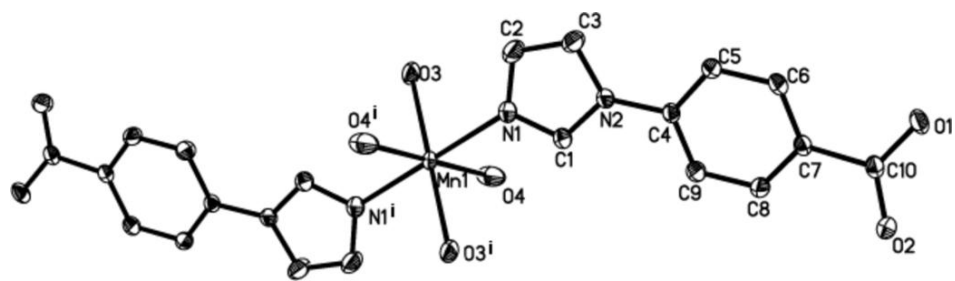


Fig. 2

